8.1. Summary of the Present Work

In the present thesis work, we have investigated the structural, magnetic, phase transitions and physical behaviors of $R_{1-y}Ba_yMn_{1-x}Ti_xO_3$ (R = La, Nd) perovskite manganites. The chemical auto-combustion method followed by calcination at various temperatures has been used to synthesized the nanocrystalline and bulk samples of $R_{1-y}Ba_yMn_{1-x}Ti_xO_3$ (R = La, Nd) manganites. The phase purity and crystal structure were characterized by using powder X-ray diffraction in conjugation with Rietveld crystal structure refinement. The microstructure was characterized by scanning electron microscopy and compositional analysis was carried out by energy dispersive X-ray spectroscopy. Magnetic properties and phase transitions were investigated by magnetic field and temperature dependent magnetization measurements. The isothermal Arrott's plots (M^2 vs. H/M) analysis was used to identify the nature of the magnetic phase transition. The temperature and frequency dependent ac susceptibility measurements were carried out to identify the nature of the spin-glass transition. We have also investigated the effect of doping concentration of Ti^{4+}-ions and particle size on structural and magnetic properties of these systems.

The important findings of the present research work are summarized below:

(i) The Rietveld analysis of the structure for the $Nd_{0.7}Ba_{0.3}Mn_{1-x}Ti_xO_3$ manganites with $0 \leq x \leq 0.50$ reveals that NBMTO manganites with $x < 0.30$ crystallize into a single phase orthorhombic structure with *Imma* space group, while, for $x \geq 0.30$ the two crystallographic phases of tetragonal structure with *I*4*/mcm* and *P*4*mm* space groups coexist. The unit cell volume for *Imma* space group for $x < 0.30$ and *I*4*/mcm* space group for $x \geq 0.30$ increases and for *P*4*mm* space group decreases with increasing concentration of Ti^{4+}-ion. Further, the Rietveld structural analysis and ionic size comparison of Mn^{p+}-ions and Ti^{4+}-ions confirm that for $x \leq 0.30$, Ti^{4+}-

ions replace Mn^{4+}-ions and for x > 0.30, Ti^{4+}-ions replace Mn^{3+}-ions and creates a new Mn^{2+}-ion to maintain the charge neutrality. In contrast, the Rietveld structure refinement for the $La_{0.6}Ba_{0.4}Mn_{1-x}Ti_xO_3$ manganites with $0 \leq x \leq 0.20$ reveals that the crystal structure is single phase cubic with $Pm\bar{3}m$ space group for all the compositions. The unit cell volume for $Pm\bar{3}m$ space group increases with increasing concentration of Ti^{4+}-ion.

(ii) The temperature dependent magnetization measurements show that $R_{1-y}Ba_yMn_{1-x}Ti_xO_3$ (R = La, Nd) manganites exhibit PM to FM phase transition and Curie temperature T_C decreases non-linearly with enhancing doping concentration of Ti^{4+}-ions due weakening of DE interaction. The larger difference between the values of T_C for NBMO (T_C = 140 K) and LBMO (T_C = 335 K) is found due to huge difference in the variance between the ionic radii of A-site cations. The experimental value of effective PM moment for NBMTO estimated from the temperature dependent inverse susceptibility plots also decreases non-linearly, as compared to theoretical value with increasing concentration of Ti^{4+}-ions, due to presence of inhomogeneous magnetic state above T_C. In contrast, for LBMTO system, effective PM moment increases exponentially due to increase of FM ordering in the PM region. The bulk sample of LBMTO-08 manganite exhibits Griffiths phase in the temperature range 212 K ≤ T ≤ 310 K with critical exponent λ_{GP} = 0.95(1) and critical temperature for random ferromagnet T_C^R = 247.7 K.

(iii) The field dependent magnetization measurements illustrate the presence of FM and AFM orderings in $R_{1-y}Ba_yMn_{1-x}Ti_xO_3$ (R = La, Nd) manganites. The FM ordering decreases and AFM ordering increases with increasing concentration of Ti^{4+}-ions. The experimental value of saturation moment reduces with the enhancement in Ti^{4+}-ions concentration. The analysis of the isothermal Arrott's plots reveals that

$R_{1-y}Ba_yMn_{1-x}Ti_xO_3$ (R = La, Nd) manganites undergo first order magnetic transition in low field region and second order magnetic transition in higher field region. The temperature and frequency dependent ac susceptibility measurements show various anomalies below room temperature corresponding to different magnetic transitions.

(iv) Analysis of the HR-SEM micrographs and EDS spectra for $Nd_{0.7}Ba_{0.3}Mn_{1-x}Ti_xO_3$ manganites with x = 0.40 and 0.50 reveals the appearance of two distinct microstructures in same sample accompanied with the compositional redistribution of the constituent elements. Dielectric measurement for $Nd_{0.7}Ba_{0.3}Mn_{1-x}Ti_xO_3$ manganites with x = 0.40 and 0.50 show very high dielectric constant ~10^5 at lower frequencies. The dielectric loss significantly decreases with increasing Ti^{4+}-ions content from x = 0.40 to x = 0.50.

(v) Magnetic field dependence of magnetization at 10 K for bulk $La_{0.6}Ba_{0.4}Mn_{1-x}Ti_xO_3$ manganites with $0 \leq x \leq 0.08$ reveals spin-orbit coupling. This spin-orbital coupling decreases with increasing doping concentration of Ti^{4+}-ions. The spin-orbital coupling in bulk $La_{0.6}Ba_{0.4}MnTiO_3$ completely disappears when particle size is reduced to nanometric range.

(vi) Effect of particle size on the structural and magnetic properties of $Nd_{0.7}Ba_{0.3}Mn_{1-x}Ti_xO_3$ manganite with x = 0.10 is investigated in detail. The crystallite and particle size increase exponentially with increasing calcination temperature. However, lattice strain decreases linearly with increasing particle size. The Rietveld refinement of the structure reveals that unit cell volume increases with increasing particle size. Temperature dependent magnetization measurements show PM to FM transition in all the samples and Curie temperature T_C decreases with increasing particle size of the samples. However, the sample calcined at 1000 ^oC, with particle size 90 nm, display unusually highest value of T_C. In low-temperature region,

NBMTO-10 manganite exhibits FM to AFM transition. The value of saturation moment increases with increasing particle size. The analysis of the temperature and frequency dependent ac susceptibility shows metallic spin-glass behavior. The nano sample of NBMTO-10 manganite calcined at 800°C (C8) exhibits Griffith's Phase like behavior in the temperature range 93 K ≤ T ≤ 160 K with critical exponent $\lambda_{GP} = 0.926(1)$ and $T_C^R = 80.4$ K.

8.2. Suggestions for Future Work

Our investigations on $R_{1-y}Ba_yMn_{1-x}Ti_xO_3$ (R = La, Nd) perovskite manganites have revealed several interesting and new aspects linked with structural and magnetic phase transitions of these new perovskite manganites. There are many things to be settled in future investigations. Few important suggestions for the future investigations are given below:

1. High-resolution neutron powder diffraction measurement should be carried out to study the magnetic structure of $Nd_{0.7}Ba_{0.3}Mn_{1-x}Ti_xO_3$ and $La_{0.6}Ba_{0.4}Mn_{1-x}Ti_xO_3$ manganites.
2. Low-temperature crystal structure analysis should be carried out for both the systems to investigate crystallographic phase transitions in $Nd_{0.7}Ba_{0.3}Mn_{1-x}Ti_xO_3$ and $La_{0.6}Ba_{0.4}Mn_{1-x}Ti_xO_3$ manganites.
3. Atomic pair distribution function (PDF) analysis should be carried out to understand structural and magnetic behaviors of $Nd_{0.7}Ba_{0.3}Mn_{1-x}Ti_xO_3$ and $La_{0.6}Ba_{0.4}Mn_{1-x}Ti_xO_3$ manganites considering local structure.
4. Magnetocaloric characterization of the $Nd_{0.7}Ba_{0.3}Mn_{1-x}Ti_xO_3$ and $La_{0.6}Ba_{0.4}Mn_{1-x}Ti_xO_3$ manganites should be done to explore the technological applications.

5. The colossal magnetoresistance (CMR) characterization should be carried out for $Nd_{0.7}Ba_{0.3}Mn_{1-x}Ti_xO_3$ and $La_{0.6}Ba_{0.4}Mn_{1-x}Ti_xO_3$ manganites.
6. The imaginary part of the temperature and frequency dependent ac susceptibility measurements show several anomalies for $La_{0.6}Ba_{0.4}Mn_{1-x}Ti_xO_3$ manganites. The origin of these anomalies should be investigated systematically in future.
7. The origin of appearance of two distinct microstructures in same sample of $Nd_{0.7}Ba_{0.3}Mn_{1-x}Ti_xO_3$ manganites with x = 0.40 and 0.50 should be investigated in future.